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EXPERIMENTAL STUDIES OF THE FORMATION/DEPOSITION  
OF SODIUM SULFATE IN/FROM COMBUSTION GASES

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## 1. INTRODUCTION, MOTIVATION

The development of gas turbines is currently impeded by high temperature ("hot") corrosion of components resulting from inorganic salts (e.g.  $\text{Na}_2\text{SO}_4$ ) in the combustion products (LOWELL, et al. (1976); HART and CUTLER (1973)).\* Engine operating experience and captive engine tests have provided valuable clues to the overall phenomenon, but small scale laboratory experiments under more precisely controlled conditions will be essential to obtain an understanding of the mechanism of disposition and hot corrosion; on which future control measures can be based.

Two aspects of the overall problem are being studied in the present program: a) processes governing the availability of sodium for  $\text{Na}_2\text{SO}_4$ -formation and b) processes governing the  $\text{Na}_2\text{SO}_4$  deposition rate on surfaces immersed in combustion products. If these can be understood specific and effective control measures may be identified to suppress the hot-corrosion problem without sacrificing other desirable performance characteristics.

Considering the second problem first (deposition), abundant and precise burner rig deposition rate data are required to develop a successful deposition rate theory relating the laboratory and engine environments (KOHL et al. (1977)). As a corollary, new experimental techniques are required to acquire such a data base. Until the present work (Section 2) dew points and deposition rates were inferred from lengthy post-mortem weighings/chemical analysis of platinum foil targets maintained for long periods in laboratory burner rigs intended for materials screening experiments (KOHL et al. (1977), STECURA (1976)).

Second, there is considerable uncertainty about the mechanism and kinetics of  $\text{Na}_2\text{SO}_4$ -formation (STEARNS et al. 1977). While it is thought that  $\text{NaCl}(c)$  first vaporizes and its sodium is released via gas phase reactions between the resulting  $\text{NaCl}$  vapor and atomic hydrogen (cf. e.g. HASTIE(1975)), the kinetics of these "elementary" steps, or possibly important rivals to them, have until the present work not been explored.

In Sections 2 and 3 specific experiments under well-defined laboratory conditions are described to answer these questions. These experiments, taken together with (i) necessary ancillary data on thermodynamic parameters (KOHL et al. (1975)) (ii) a theoretical framework for predicting dew points and deposition rates (ROSNER (1977), KOHL et al. (1977)), and (iii) follow-on experiments directed at the molecular transport properties of sodium-containing gaseous species, should put the prediction of sulfate formation/deposition phenomena on a much firmer footing.

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\*Similar problems are being encountered in the development of magneto-gas-dynamic energy conversion devices which operate with alkali metal seeds and sulfur-containing fuels (e.g. pulverized coal).

## 2. BURNER EXPERIMENTS ON DEW POINTS AND DEPOSITION RATE VIA REMOTE OPTICAL METHODS<sup>†</sup>

### 2.1 Background

Precise measurements of dew points and deposition rates of inorganic salts formed in combustion product gases are essential to obtain an improved understanding of corrosive salt formation and deposition in gas turbines. Improved measurements would provide data to test the accuracy and domain of validity of the recently developed multicomponent boundary layer theory (ROSNER *et al.* (1978)), and in the evaluation of future control strategies.

KOHL *et al.* (1977) made gravimetric measurements of  $\text{Na}_2\text{SO}_4$  deposition on cylindrical platinum targets exposed to the products of a liquid fuel/air atmospheric pressure combustor. Salt solutions were injected into the combustion chamber through a pump-fed aspirator system. Our purpose is to obtain dew point and deposition rate data of improved precision under better-controlled laboratory conditions. To accomplish this we are exploiting monochromatic laser light to probe condensation onset, and condensate film growth (via interference of reflected light) on electrically heated ribbons immersed in seeded, flat flame combustion product gases. As outlined by ROSNER (1977) the sudden reduction of ribbon heating current would cause a ribbon to radiatively cool through the prevailing dew point, and the condensate onset temperature can be obtained "on the fly". Subsequent deposition rates under these seeding conditions can be obtained from the spacing of intensity maxima in the reflected monochromatic light from liquid condensate films in the submicron (say,  $10^{-1}$  to  $10^0 \mu\text{m}$ ) range.<sup>†</sup> To make future measurements using ellipsometric techniques, a linearly polarized laser has been obtained.

Our strategy during the first year of this program has been to demonstrate these techniques using a deliberately simple experimental system. Since gases can be more accurately metered into the burner than liquids, we have used boron trichloride as the seed gas in these preliminary experiments. Boric oxide ( $\text{B}_2\text{O}_3$ ) is formed in such a flame, and the corresponding dew point and deposition rates of this oxide have been accurately measured using the abovementioned technique. The results of this set of experiments will be used to demonstrate the proposed experimental techniques and allow us to test the accuracy of chemically frozen boundary layer theory (ROSNER *et al.* (1978)).

### 2.2 Experimental Techniques

Remote optical methods can be used for measuring dew points, and deposition rates of inorganic salts on surfaces exposed to seeded combustion gases (SESHADRI and ROSNER (1978)). Such measurements can be made either by recording interference in a reflected beam of monochromatic light, or by measuring the change in polarization upon reflection. As noted above, to demonstrate the interference method a deliberately simple experimental system was used, in which an electrically heated platinum

<sup>†</sup>McINTYRE and McTAGGART (1970) used interference in reflected sodium lamp radiation to study solid iodide film growth on silver. SUGAWARA, *et al.* (1973) exploited the interference technique to study silicon dioxide ( $\text{SiO}_2$ ) growth rates on silicon wafers using He-Ne laser radiation.

<sup>†</sup>Prepared by Drs. K. Seshadri and D.E. Rosner



ribbon was immersed in seeded flat-flame combustion product gases. When boron trichloride, a gas at STP, is used as the seed material boric oxide ( $B_2O_3$ ) is formed in the flame and its dew point and growth rate can then be measured using the interference technique. The apparatus in its present form (cf. Fig. 2.2-1) consists of a) an optical system, b) an electrical system (for heating the target, and measuring its temperature) c) the burner assembly, and d) the gas feed systems. Only a brief discussion of the apparatus and experimental procedure is given here. For further details consult SESHADRI and ROSNER (1978).

A linearly polarized helium-neon laser is used as a source of monochromatic light ( $0.6328 \mu m$ ). The beam reflected from the target is then focused on the aperture of a photometer whose output is recorded on a strip chart potentiometer.

The target is a platinum ribbon (50 mm long, 6 mm wide, 0.127 mm thick) held above the burner by two copper rods. The ribbon is electrically heated by connecting the copper rods to a 50 amp (max) dc-power supply. The electrical resistance of a 4 mm wide central section of the ribbon is measured using two platinum "tap" wires of 0.127 mm diameter spot-welded to the ribbon. The temperature of the ribbon is then calculated from the known value of its electrical resistance.

The burner consists of a stainless steel tube of 2.54 cm inner diameter, 7.62 cm long. A premixed gaseous stream of fuel (propane), air, and the seed vapor is fed to the burner at the bottom of the tube. Variable area flowmeters are used to measure individual gas flow rates. To obtain a laminar flow of the premixed gases with a uniform velocity above the burner, a porous monel disk 2.54 cm diameter, and 1.27 cm thick is placed at the top of the tube.

To measure boric oxide deposition rates by the interference method, the ribbon was positioned at approximately 3.8 cm from the surface of the burner. Flow rates of air and propane were adjusted to obtain a blue, stable, flat-flame. Initially the electrical current flowing through the ribbon was maintained high enough for the temperature of the ribbon to be a few hundred degrees above the dew point of boric oxide at the anticipated  $BCl_3$ -seed level. The seed gas is then turned on, at which point the flame was visually observed to turn green. The heating current to the ribbon is then reduced to bring the ribbon below the  $B_2O_3$ -dew point. A sharp decrease in the intensity of the reflected light is observed at the instant of oxide condensation. As the oxide film grows, the light reflected from the outer surface of the growing oxide layer and from the ribbon surface undergoes constructive and destructive interference, causing a modulated intensity in the collected beam. The corresponding film growth rate is calculated from the spacing between intensity maxima, using the known chart recorder speed. The ribbon heating current is then increased to evaporate the oxide layer, and the experiment repeated to obtain the growth rate at a different target temperature. The composition of the film was analyzed on a Hewlett-Packard Model 5950 ESCA Spectrometer system, and confirmed to be boric oxide.

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Uncertainties in target temperature measurement are expected to be less than  $\pm 10^\circ K$ , and the inaccuracies in obtaining the growth rate are expected to be less than +5%. Deposition rates reported here are based on the room temperature refractive index of  $B_2O_3$  (1.458).

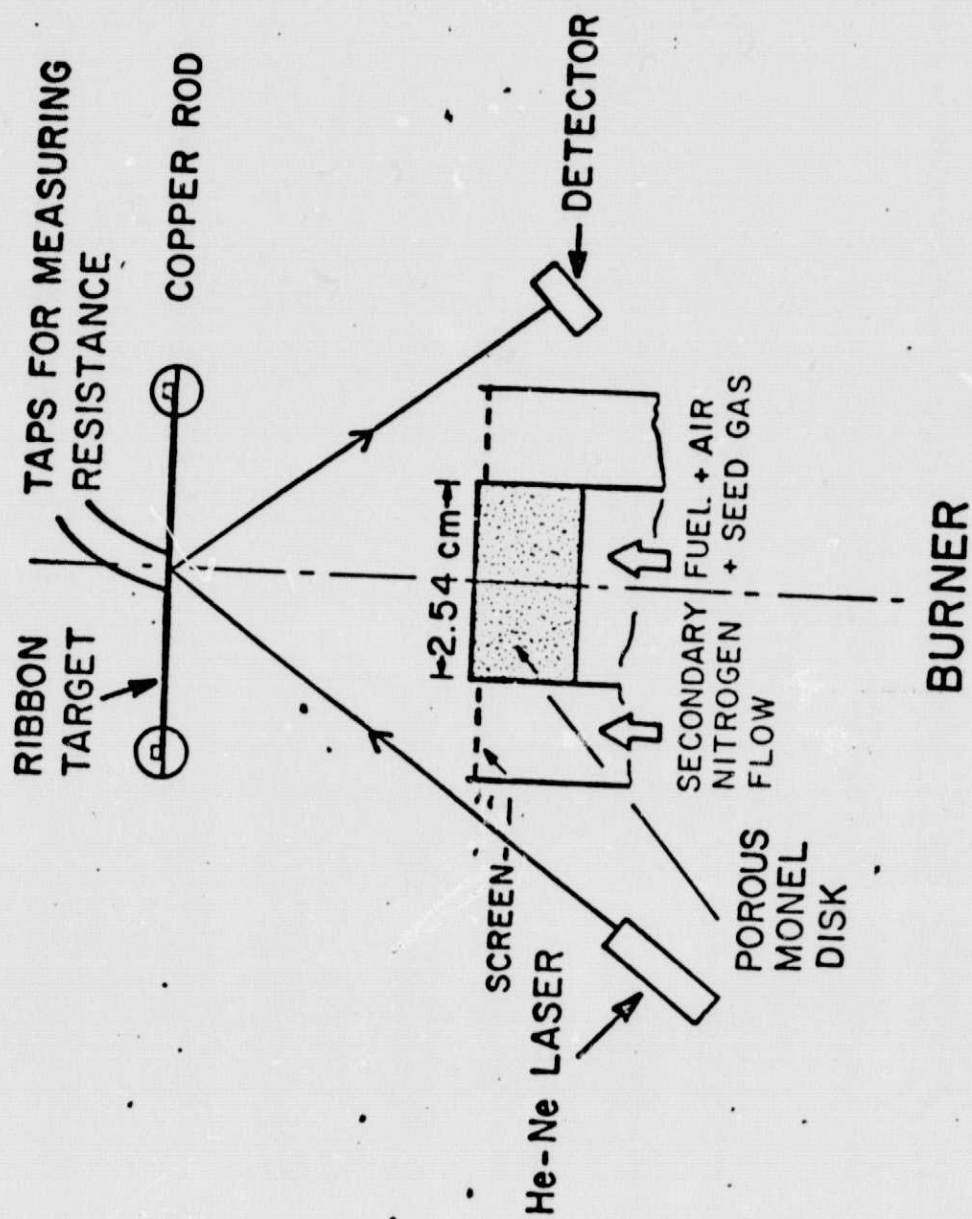


Fig 2.2-1

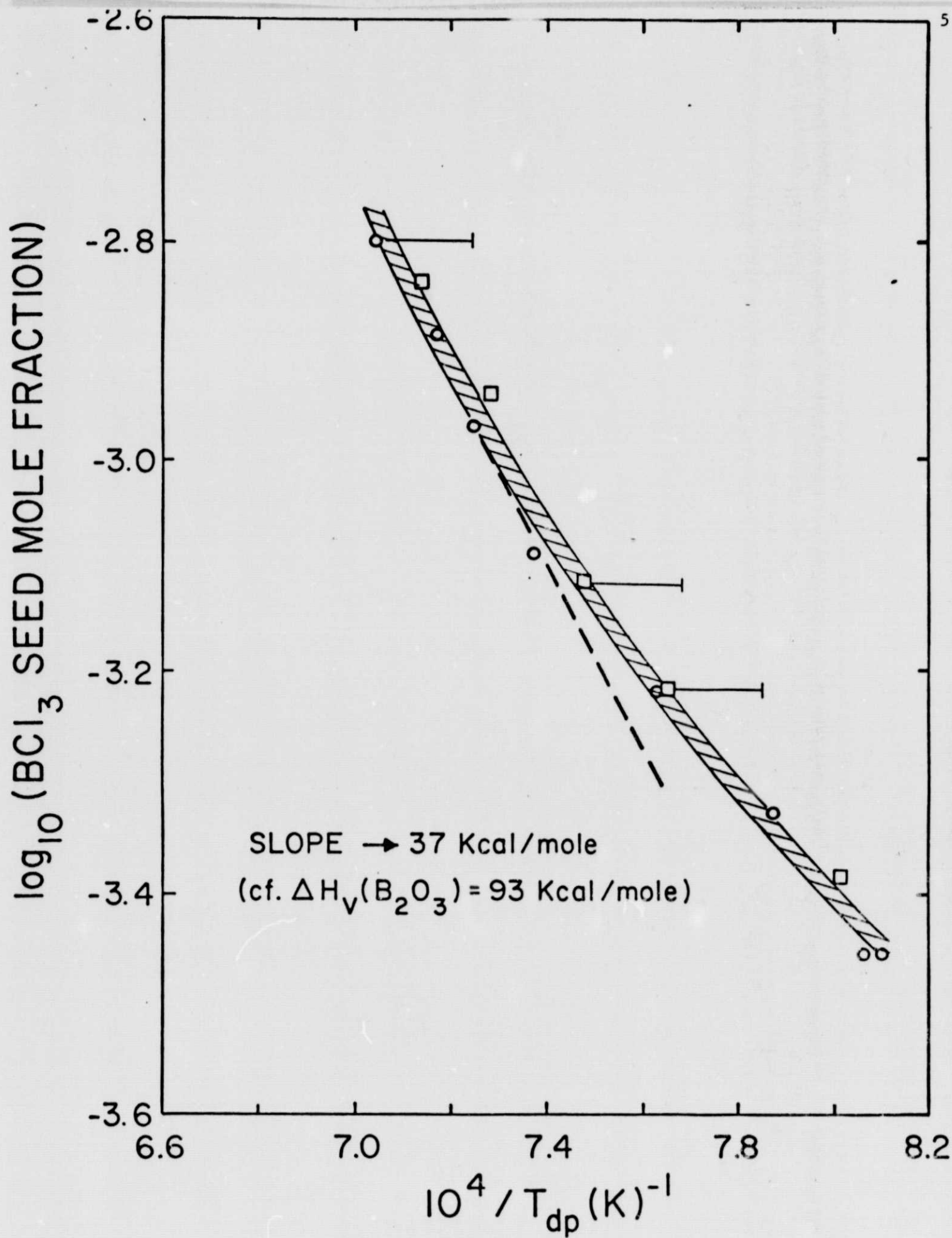
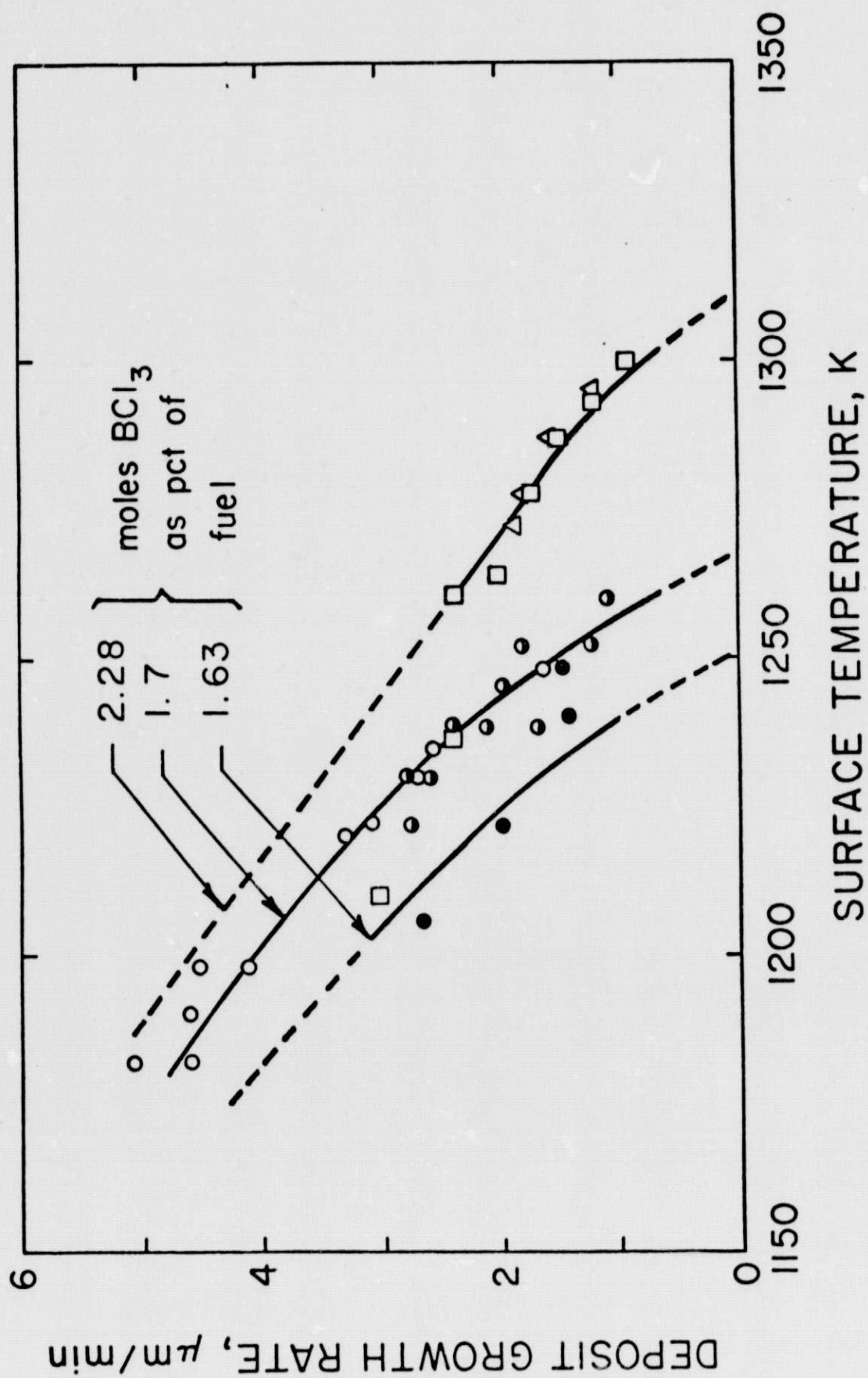


Fig 2.3-1



*Fig. 2.3-2*

### 2.3 Preliminary Results

Our preliminary results at different  $\text{BCl}_3$  seed levels, but for one flow velocity and equivalence ratio (.813) are presented here. The  $\text{B}_2\text{O}_3$  dew point,  $T_{dp}$ , defined as the target temperature at which the growth rate extrapolates to zero, is found to increase with increasing seed level. In Fig. 2.3-1 we show a plot of  $\log(\text{BCl}_3)$  vs  $1/T_{dp}$ , at an equivalence ratio of (.813). Interestingly enough, the nominal slope of this plot corresponds to a value of only 37 kcal/mole for the "effective" heat of vaporization of  $\text{B}_2\text{O}_3(l)$ , substantially below the true value (93 kcal/mole) for this oxide. To investigate this phenomenon more thoroughly similar measurements are being made at equivalence ratios near unity. These measurements appear to give an intermediate value for the effective heat of vaporization of  $\text{B}_2\text{O}_3$ , suggesting again that in the present system the observed dew points are strongly influenced by chemical kinetic phenomena.

Results for the  $\text{B}_2\text{O}_3$  deposition rates at surface temperatures below the above-mentioned dew points are collected in Fig. 2.3-2. In the next reporting period we intend to compare these observed rates with those expected based on multicomponent chemically frozen boundary layer theory (ROSNER, D.E., CHEN, B.K., et al. (1978)).

## 3. ATOM ATTACK OF SOLID ALKALI HALIDES<sup>†</sup>

### 3.1 Introduction

The aim of this phase of our present study is to obtain information on the kinetics and mechanism of heterogeneous reactions capable of releasing alkali metal vapors from these stable halide salts ( $\text{NaCl}$ ,  $\text{KCl}$ ). Because of the importance of gaseous  $\text{Na}(g)$  as a precursor to  $\text{Na}_2\text{SO}_4(c)$  formation, these data should allow us to evaluate alternatives to mechanisms involving  $\text{NaCl}(c)$  sublimation as a first step.

We are currently carrying out a kinetic and stoichiometric study of these reactions using atomic absorption and/or emission spectroscopy combined with microwave discharge-vacuum flow reactor techniques at moderate temperatures. The preliminary results summarized below indicate the direct attack of solid alkali halides ( $\text{NaCl}$  and  $\text{KCl}$ ) by atomic hydrogen or atomic oxygen indeed produces alkali atoms, even at surface temperatures as low as at 550°K. At this temperature, sublimation is negligible, hence gas phase (homogeneous) reactions involving  $\text{NaCl}(g)$  or  $\text{KCl}(g)$  should play no role in the observed alkali vapor production.

### 3.2 K(g) Release via the Direct H(g)/KCl(s) Reaction

Following up our measurements of  $\text{Na}(g)$  production via the  $\text{H}(g)/\text{NaCl}(s)$  reaction (Semi-Annual Report 1, Section 3), preliminary measurements have been made on the analogous  $\text{H-atom/KCl}(s)$  reaction, with the results indicated below.

†

Prepared by Drs. P-D Foo and D.E. Rosner

Analytical grade potassium chloride was first melted in a flame and its vapor condensed on a slowly rotating quartz tube with outside diameter 3 mm. A KCl(s) sample layer approximately 0.2 mm thick x 4 mm long was used for this study. The sample was heated by an electrical resistor located inside the quartz tube.

Potassium atoms produced by the  $H(g)/KCl(s)$  reaction in the temperature range 580–640° K were detected by an atomic fluorescence technique. For this purpose 0.25 m monochromator at 766 nm was used, coupled to a photomultiplier/recording potentiometer combination.

Our preliminary results indicate that when potassium chloride is heated to 580 K or higher and exposed to a stream containing atomic hydrogen, an appreciable emission intensity at 766 nm appears. The emission occurs as soon as the heated KCl is exposed to the atomic hydrogen stream and disappears immediately when the atomic hydrogen stream is interrupted either by turning off the microwave discharge or hydrogen gas flow. Typical results for the emission intensity  $I$  of  $K^*(g)$  at 766 nm versus surface temperature  $T$  are shown on the  $\ln I$

vs.  $T^{-1}$  plane in Fig. 3.2-1. The apparent activation energy for excited alkali atom formation is seen to be about 24 Kcal/mole, which should be compared with the corresponding value (SA1, Section 3) of 5.2 Kcal/mole for the  $H/NaCl(s)$  reaction. Further discussion of the mechanism and thermodynamics of these reactions will be postponed until the completion of gravimetric measurements currently in progress.

### 3.3 Alkali Atom Release via $O(g)/$ Alkali Halide(s) Reactions

Though the thermodynamics would appear to be less favorable, the relative abundance of O-atoms as intermediates in fuel-lean hydrocarbon/air combustion led us to examine the corresponding alkali chloride reactions with atomic oxygen. Remarkably enough, readily detectable  $Na^*(g)$  and  $K^*(g)$  -atoms have been observed in emission (at 589 nm and 766, 769 nm, respectively).

Atomic oxygen was produced by passage of a 10%  $O_2$ , 90% Ar mixture through a 2450 MHz microwave discharge cavity. Ultra high purity grade oxygen and argon (Matheson Gas Co.) was used without prior treatment. O-atom concentrations were determined by the  $NO_2$  chemiluminescent titration method.

Our experimental setup for studying the  $O(g)/$ alkali chloride reactions is very similar to that described in SA 1 (Section 3) for the corresponding H-atom heterogeneous reactions. However in this study, a thin platinum foil, 0.127 mm thick 4 mm wide and 20 mm long was used as the sample holder. A small amount of crystalline NaCl or KCl, was placed on the platinum foil and electrically heated until molten, thus



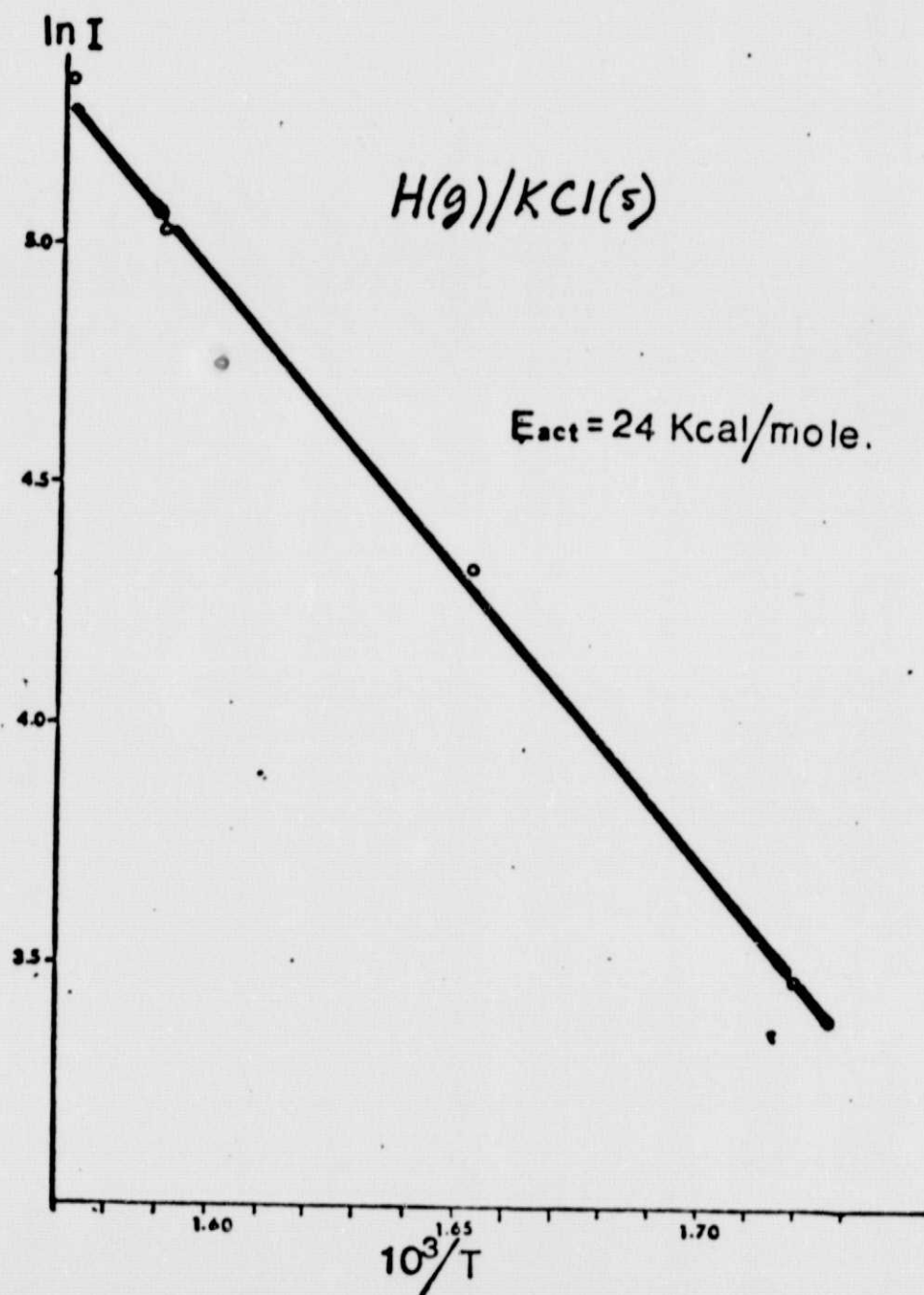


Fig. 3.2-1

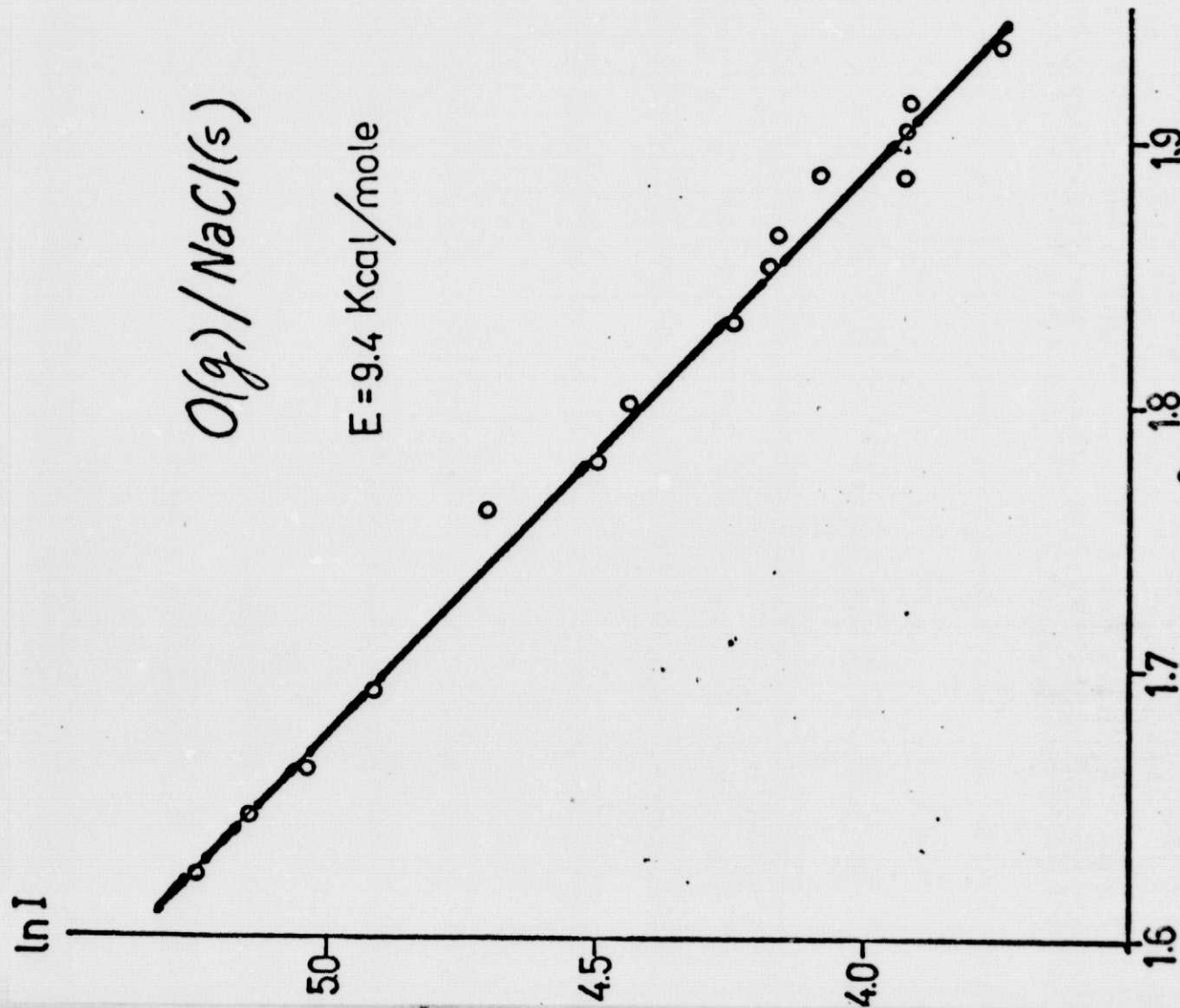
forming a thin layer of salt. The sample temperature was measured using a Pt/Pt-Rh thermocouple spark welded to the foil. The heated alkali chloride/platinum sample was exposed to a cross flow of atomic oxygen stream. When NaCl and KCl samples were thus heated and exposed to atomic oxygen stream, alkali atom emission peaks appeared downstream of the ribbon. Moreover, the emission intensity systematically increased with surface temperature in accord with an Arrhenius (constant activation energy) process (see Figs. 3.3-1,2). Another possible reaction product in these reactions is, of course, ClO(g) (with a bond energy of 63.33 Kcal/mole at 0°K) however direct detection of this diatomic species is beyond the scope of the present program. Further study of these remarkable atom/alkali halide interactions will be included in the follow-on experimental program. Of particular interest will be estimates of their possible role in the formation of alkali sulfate precursors under aircraft gas turbine combustor conditions.

#### 4. ADMINISTRATIVE INFORMATION

Our initial objectives of demonstrating the use of a remote optical technique (interference) to determine dew points and deposition rates in seeded flames have been achieved, along with preliminary results on sodium atom release from NaCl(s) by direct H-atom attack. Our current research status is documented in Sections 2 and 3 of this report, as well in our recent paper presented at the 10th Materials Research Symposium (ROSNER, SESHADRI et al. (1978)). Earlier progress reports were made on our visit to NASA Lewis Research Center (June 20, 1978) and during the visit to Yale of Drs. F. Kohl and C.A. Stearns (July 12, 1978). Summary memos on each of these sessions were independently transmitted to Dr. F. Kohl. To apply our optical interference measurements to alkali sulfates, introduce the polarization method, and extend our measurements on direct radical attack on NaCl(s) we submitted a renewal proposal to NASA-LeRC on July 28, 1978, leading to the follow-on research program (commencing November 16, 1978). A full-length journal paper on our optical interference technique applied to B<sub>2</sub>O<sub>3</sub> film growth from BCl<sub>3</sub>(g)-seeded flames is now being prepared and should be issued early in 1979.

The author has also participated in two conferences at which work relevant to the present program has been discussed: (1) the Gordon Research Conference on High Temperature Chemistry, (August 7-11 (1978), Wolfboro, N.H.) and the 2nd. International Conference on Physicochemical Hydrodynamics (The Levich Conference), November 6-8 (1978), Washington DC.





Mention should be made of the combination dc power supply/temperature controller/relay rack requested in my letter of 7/28/78. This package arrived (damaged\*) at Yale on 10/12/78 and was inspected on 11/1/78 by Peter O'Callaghan, (Interstate Inspections, 91 Giddings Ave. Windsor, Ct. 06095, (203) 688-5876) who abruptly departed from our laboratory without submitting his accident report. If insurance reimbursement (for repairs) is not received via Cooper-Jarrett Inc. in this clear-cut case I recommend that neither Yale nor NASA use this transportation company for future shipments of scientific equipment.

As documented in the first Semi-Annual on this grant, the experimental results contained in Sections 2, 3 are primarily due to Drs. K. Seshadri and P-D. Foo, respectively. Much of the six month progress reported above would not have been possible without the valuable inputs of our HTRC Laboratory colleagues, especially Drs. P.C. Nordine, B. Halpern, and R. Atkins.

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\*US Govt. Bill of Lading K-4540967 Issued 9/27/78.

The entire wooden crate (29x31x62 in., 430 lb.) appears to have been dropped (ca. 5-10 ft?) causing extensive bending of cantilevered parts.

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